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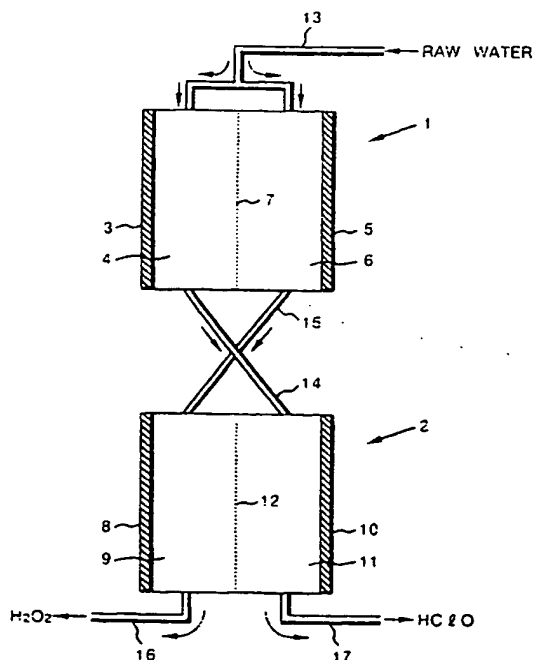
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(54) Process and apparatus for the production of electrolyzed water

(57) Electrolyzed functional water is produced by a two stage electrolysis. There is a first electrolyzing step of continuously feeding water containing electrolyte to an electrolytic cell (1) equipped with an anode (3), a cathode (5) and an ion permeable membrane (7) therebetween to electrolyze it and a second electrolyzing step of subjecting to electrolysis, in the anodic side (9) of an electrolytic cell (2) equipped with an anode (8), a cathode (10) and an ion permeable membrane (12) therebetween, an electrolyte which is electrolyte to be found in the cathodic side (6) of the electrolytic cell (1) of the first electrolyzing step after water fed to said cell has been electrolyzed. Electrolyzed functional water is withdrawn from the anodic side (9) used in the second electrolyzing step after water in this side has taken part in electrolysis in the second electrolyzing step.

FIG. 1



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## Description

The present invention relates to the production of electrolyzed functional water having oxidizing ability, which is suitable for use in general sterilization and disinfection, sterilization and disinfection of soil, crops and plants, and the like, and to apparatus which can be used in the production of such water.

There has heretofore been known a process in which raw water containing a chloride such as sodium chloride (NaCl) and/or potassium chloride (KCl) as electrolyte is fed to an electrolytic cell equipped with an anode, a cathode and an ion-permeable membrane between them to electrolyse it, thereby producing electrolyzed functional water at the anodic side, which is suitable for use as a bactericide, a sterilizer and a disinfectant.

In the above conventional process, the electrolyzed functional water obtained from the anodic side contains electrolyzed products such as chlorine ( $\text{Cl}_2$ ), hypochlorous acid ( $\text{HClO}$ ), chlorine oxide ( $\text{ClO}^\cdot$ ) and the like.

The electrolyzed functional water has strong sterilizing ability because of the chlorine, chlorine oxide and hypochlorous acid in particular.

However, the electrolyzed functional water obtained by the conventional production process has the disadvantage of insufficient bactericidal effect against chlorine-resistant germ, because its sterilizing ability is due to the above-described chlorine or chlorine compounds.

Further, the electrolyzed functional water has a high concentration of chlorine with a low pH at the same time, so that it tends to give off toxic chlorine gas into the atmosphere. Therefore, it is necessary to take care to use it in a closed room or the like.

Accordingly, it is an object of the present invention to provide a process for providing electrolyzed functional water, in which the aforesaid disadvantages of prior procedures may be reduced or even eliminated.

In one aspect, this invention provides a first process for producing electrolyzed functional water which comprises:-

a first electrolyzing step of continuously feeding water containing electrolyte to an electrolytic cell equipped with an anode, a cathode and an ion permeable membrane therebetween to electrolyse it,

a second electrolyzing step of subjecting to electrolysis, in the anodic side of an electrolytic cell equipped with an anode, a cathode and an ion permeable membrane therebetween, an electrolyte which is electrolyte to be found in the cathodic side of the electrolytic cell of the first electrolyzing step after water fed to said cell has been electrolysed,

and withdrawing electrolyzed functional water from the anodic side used in the second electrolyzing step after water in said side has taken part in electrolysis in said second electrolyzing step.

In a first process embodying the invention, the second electrolyzing step is carried out on the electrolyzed water obtained on the cathodic side of the electrolytic cell used in the first electrolyzing step, which electrolyzed water is continuously withdrawn from the cathodic side of said electrolytic cell and continuously fed to the anodic side of a second electrolytic cell in which it is subjected to the second electrolyzing step, and the electrolyzed functional water is continuously withdrawn from the anodic side of the second electrolytic-cell.

The electrolyzed functional water can also be produced by a second process embodying the present invention. Here, after carrying out of the first electrolyzing step on water fed to the electrolytic cell, the polarities of the cell are reversed and the second electrolyzing step then comprises conducting electrolysis of the then existing contents of the electrolytic cell and is followed by the withdrawal of electrolyzed functional water from the side of the cell which is the anodic side in the second electrolyzing step.

Usually, natural water can be electrolyzed because of containing various kinds of ions such as chloride, sulfate, sodium, potassium ions, etc.

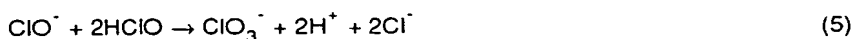
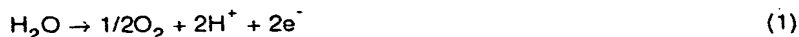
Accordingly, in the present invention, any water such as tap water, industrial water or well water may be used as the raw water for electrolysis provided that it contains some electrolytes. However, it is preferable to add electrolyte such as a chloride for successful electrolysis.

Sodium chloride (NaCl) or potassium chloride (KCl) are preferably added as electrolytes. Sodium chloride is very low cost, while potassium chloride causes the electrolyzed functional water to contain potassium which is useful as a fertilizer when the electrolyzed functional water is used as a soil disinfectant.

Electrolytes added to water are preferably added in a concentration ranging from 0.001 to 1 mol/liter. If the concentration is lower than 0.001 mol/liter, it is not enough to improve the electrolyzing efficiency. On the other hand, if the concentration is higher than 1 mol/liter, the electrolyzing efficiency is not improved markedly, and a large amount of electrolytes remains in electrolyzed water formed to be a problem when the electrolyzed functional water is used.

According to the production process of the first and second aspects of the present invention, first of all, water is electrolyzed to generate oxygen ( $\text{O}_2$ ) and a hydrogen ion ( $\text{H}^+$ ) on the anodic side of the electrolytic cell in the first electrolyzing step. When water contains a chloride (i.e. chloride ions), the chloride ions ( $\text{Cl}^-$ ) are oxidized to generate chlorine ( $\text{Cl}_2$ ), and a part of the chlorine is dissolved in water to produce chlorine compounds (including ions) such as

hypochlorous acid, while the other part thereof and the generated oxygen are liberated into the atmosphere as gas from the electrolytic cell. The reactions on the anodic side of the electrolytic cell are as follows:

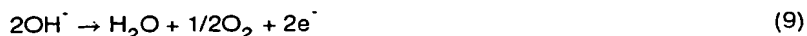
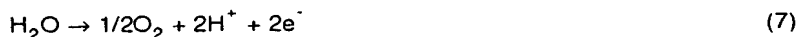


On the cathodic side, on the other hand, water is electrolyzed to generate hydrogen and a hydroxide ion ( $\text{OH}^-$ ). The reaction on the cathodic side of the electrolytic cell is as follows:



As a result, acidic water containing chlorine and chlorine compounds is obtained from the anodic side of the electrolytic cell, while alkaline water is obtained from the cathodic side.

When the alkaline electrolyzed water obtained from the cathodic side in the first electrolyzing step is then electrolyzed again on the anodic side of an electrolytic cell in the second electrolyzing step, oxygen is generated, and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and oxygen are produced from hydroxide ions. The reactions at the anodic side in the second electrolyzing step are as follows:



As a result, the electrolyzed functional water according to the present invention is obtained from the anodic side of the electrolytic cell in the second electrolyzing step.

The electrolyzed functional water according to the present invention has strong oxidizing ability due to nascent oxygen ( $[\text{O}]$ ), peroxide and OH radicals ( $\cdot\text{OH}$ ) generated from hydrogen peroxide, so that it has excellent effects on sterilization, disinfection, deodorization and the like. In addition, the above hydrogen peroxide, superoxide and OH radicals can be expected to have a bacterial effect against chlorine-resistant germs.

Further, the hydrogen peroxide is decomposed into only oxygen and water ( $\text{H}_2\text{O}$ ), and so it is not toxic and is safe even after the reaction. Therefore, the electrolyzed functional water according to the present invention can also be used in sterilization and disinfection of tableware and the like.

Incidentally, when chloride is present as an electrolyte in the raw water, the chloride ions remain in the alkaline water obtained at the cathodic side of the electrolytic cell in the first electrolyzing step, and so small amounts of chlorine, hypochlorous acid and the like are produced from the chloride ions as shown in reaction (10) in the anodic side of the cell in the second electrolyzing step.

Accordingly, the electrolyzed functional water contains small amounts of the chlorine compounds.

However, chlorine compounds are unavoidably produced from the remaining chloride ions in the alkaline water by electrolysis, and so the residual chlorine concentration is low. Therefore, the electrolyzed functional water according to the present invention gives off a small amount of chlorine gas even when the chloride is present as the electrolyte in the raw water.

On the other hand, hydrogen peroxide is relatively stable in an acid region, and on the contrary hypochlorous acid has high activity against bactericidal action and the like in the acid region. Further, any hydrogen peroxide in the alkaline region is more active and hypochlorous acid is relatively stable. It is further expected that the OH radicals are produced by the interaction of hypochlorous acid and hydrogen peroxide. Accordingly, the electrolyzed functional water according to the present invention is expected to have a synergistic effect on the strength of small amount of chlorine compounds and the hydrogen peroxide when a chloride is present as the electrolyte in the raw water.

According to the production process of the first above defined process embodying the present invention, the raw water continuously fed to the first electrolytic cell is electrolyzed in the first electrolyzing step, and the alkaline electrolyzed water is continuously withdrawn from the cathodic side of the first electrolytic cell. The electrolyzed water is then continuously fed to the anodic side of the second electrolytic cell and electrolyzed in the second electrolyzing step, whereby the electrolyzed functional water according to the present invention can be continuously taken out from the anodic side of the second electrolytic cell.

In such process, water supply to the cathodic side of the second electrolytic cell can be the raw water or the acidic water from the first electrolytic cell which is fed continuously into the cathodic side of the second electrolytic cell.

When chloride is present as electrolyte in the raw water, electrolyzed water containing chlorine and chlorine compounds such as hypochlorous acid is obtained on the anodic side of the first electrolytic cell. The above acidic electrolyzed water may be electrolyzed again on the cathodic side of the second electrolytic cell, with the water obtained indicating a pH range between weak acidity and weak alkalinity. The chlorine compounds, in particular, hypochlorous acid is known to be stable and to exhibit a bleaching action and a bactericidal action in the alkaline region. In the second electrolyzing step, it is possible to control the pH of the electrolyzed water formed to some extent by adjusting the intensity of electrolysis, so that the pH of the electrolyzed water containing the chlorine and the chlorine compounds such as hypochlorous acid can be controlled to be weakly alkaline.

Accordingly, in the case where chloride is present as electrolyte in the raw water, according to the production process of the first aspect, the electrolyzed water from the anodic side of the first electrolytic cell is continuously withdrawn and fed to the cathodic side of the second electrolytic cell in the second electrolyzing step, whereby an aqueous solution exhibiting a bleaching reaction can be continuously withdrawn as a by-product of the production of the targeted electrolyzed functional water from the cathodic side of the second electrolytic cell.

According to the second above-defined process embodying the present invention, the cathodic side of the electrolytic cell in the first electrolyzing step is switched to being the anodic side in the second electrolyzing step, so that there is no need to transfer the electrolyzed water obtained in the first electrolyzing step. Therefore, the production process is operated in one electrolytic cell, and the apparatus can be simplified.

According to such process, the electrolyzed water on the anodic side of the electrolytic cell in the first electrolyzing step is electrolyzed again on the cathodic side of the electrolytic cell in the second electrolyzing step without transferring the electrolyzed water. Therefore, the aqueous solution exhibiting a bleaching action can be withdrawn as a by-product of the electrolyzed functional water from the cathodic side in the second electrolyzing step when a chloride is present as the electrolyte in the raw water.

The electrolyzed functional water obtained in the process of the present invention has high oxidizing ability in the weakly acidic to weakly alkaline region and is hence easy to use, unlike the conventional electrolyzed functional water having a strong acidity. Therefore, a feature of the production process according to the first or second aspect is that an electrolyzed functional water containing hydrogen peroxide and controlled to pH range within 3.5 to 10.5 can be produced by controlling electrolysis conditions in the second electrolyzing step. The method of controlling the electrolysis conditions includes a method of controlling the quantity of electric charge applied between the anode electrode and the cathode electrode.

Further, electrolyzed functional water can also be produced by a third process embodying the present invention. In this process the water containing electrolyte is fed continuously to the cathodic side of a said electrolytic cell containing electrolyte at the anodic side thereof and undergoes electrolysis, and wherein electrolyzed water is continuously withdrawn from the cathodic side of the electrolytic cell and fed to the anodic side of the electrolytic cell to be electrolyzed further as new water containing electrolyte is fed to the cathodic side and electrolyzed there, whereby said first and second electrolyzing steps take place simultaneously in the electrolytic cell, with electrolyzed functional water being withdrawn continuously from the anodic side of the electrolytic cell.

In such third process embodying the invention hydrogen is generated and hydroxide ions ( $\text{OH}^-$ ) are formed on the cathodic side by electrolysis of the water. As a result, alkaline electrolyzed water is obtained in accordance with the reaction (6).

On the anodic side of the electrolytic cell on the other hand, oxygen ( $\text{O}_2$ ) and hydrogen ions are generated by

electrolysis of the water according to reaction (1) at the initial stage of the electrolysis. However, the acidic water produced at the initial stage of the electrolysis is quickly replaced by the alkaline electrolyzed water produced on the cathodic side because the alkaline electrolyzed water is continuously fed into the anodic side. Incidentally, when the raw water contains chloride (chloride ions) as electrolyte, the chloride ions are simultaneously oxidized into chlorine ( $\text{Cl}_2$ ) at this time.

When the raw water on the anodic side of the electrolytic cell is then completely replaced by the alkaline electrolyzed water from the cathodic side, the alkaline electrolyzed water is electrolyzed on the anodic side, and new raw water is electrolyzed on the cathodic side.

As a result, reaction (6) takes place on the cathodic side in the same manner as described above to generate hydrogen and hydroxide ions ( $\text{OH}^-$ ), while on the anodic side, as shown by the reactions (7) to (9), the electrolysis of the water takes place, and at the same time hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and oxygen are produced from the hydroxide ion contained in the electrolyzed water from the cathodic side. Then, the electrolyzed functional water according to the present invention is obtained from the anodic side.

When the raw water contains chloride (chloride ion) as an electrolyte,  $\text{Cl}^-$  (chloride ion) contained in the alkaline water fed to the anodic side is also oxidized at the same time.

Accordingly, hypochlorous acid which is in the electrolytic water obtained, and stable in a neutral pH region comes to coexist as a chlorine component. However, the diffusion of a chlorine in this pH region is smaller than that of conventional electrolyzed water.

In the first and second above-specified processes embodying the invention, the electrolyzed functional water is withdrawn from the anodic side in the second electrolyzing step after the two step electrolysis process. Therefore, half of the raw water fed is converted into the electrolyzed functional water.

In the third above specified process embodying the present invention on the other hand, once the raw water on the anodic side of the electrolytic cell is replaced by the alkaline electrolyzed water from the cathodic side, the alkaline electrolyzed water from the cathodic side is continuously fed to the anodic side after this, and so the electrolyzed functional water can be continuously withdrawn from the anodic side.

After the raw water on the anodic side is replaced by the electrolyzed water from the cathodic side, the whole quantity of the raw water fed to the cathodic side can be converted into the electrolyzed functional water containing hydrogen peroxide. Therefore, the yield of production can be enhanced.

Further in the third above-specified process embodying the present invention, the electrolysis by which the electrolyzed functional water is produced is conducted on the anodic side, and at the same time the electrolysis by which the alkaline electrolyzed water to be fed to the anodic side is produced is conducted on the cathodic side. Therefore, the yield of the electrolyzed functional water per supplied electric power is increased.

The third above-specified process can be performed by means of an apparatus which comprises an electrolytic cell equipped with two electrodes separated by an ion-permeable membrane, a water feeding means for continuously feeding water containing electrolyte to one side of the electrolytic cell containing one said electrode, an electrolyzed water feeding means for continuously feeding water electrolyzed at the electrode at said one side of the electrolytic cell to the other side of the electrolytic cell to undergo further electrolysis at the other said electrode and a take-off means for continuously withdrawing electrolyzed functional water from the side of the electrolytic cell at which the further electrolysis has occurred, in which apparatus said one electrode and the other said electrode are electrically connected to act as a cathode and an anode respectively.

When an electrolytic cell is continuously used for a long period of time, in general, the electrolytic efficiency decreases gradually, due to deposition on the electrodes of scale formed from electrolysis by-products. In order to prevent the graded reduction in the electrolytic efficiency due to the adhesion of the scale, it is only necessary to conduct electrolysis with the polarities of electric currents applied to the anode and the cathode reversed periodically, thereby removing the scale. However, such a method involves the problem that the production of the electrolyzed functional water is intermitted during the cleaning of the electrodes.

Therefore, another apparatus suitable for the third above-specified process is a modification of the above defined apparatus which has the polarities of said electrodes reversible and comprises (a) a first flow path comprising a first water feeding means for continuously feeding water containing electrolyte to the side of an electrolytic cell containing one electrode when this electrode is used as a cathode, a first electrolyzed water feeding means for continuously feeding the electrolyzed water from the side containing the first electrode to the side containing the other electrode, and a first electrolyzed functional water take-out means for continuously withdrawing electrolyzed functional water from the other side of the electrolytic cell; (b) a second flow path comprising a second water feeding means for continuously feeding water containing electrolyte to the side of the electrolytic cell containing the other electrode when the other electrode is used as a cathode, a second electrolyzed water feeding means for continuously feeding the electrolyzed water from the side containing the other electrode to the side containing the one electrode, and a second electrolyzed functional water takeout means for continuously withdrawing electrolyzed functional water from the side containing the one electrode; and (c) a change-over means for changing a flow path over to the first flow path when the one electrode

is used as a cathode or over to the second flow path when the other electrode is used as a cathode.

With an apparatus of such construction, the two flow paths are provided so as to change over the flow path according to the polarities of said both electrodes, so that the production of the electrolyzed functional water can be continued even when the polarities of said both electrodes are reversed to remove scale deposited to the surfaces of the electrodes.

In the third above-defined process embodying the present invention, as with other processes embodying the present invention, any water may be used as the raw water fed to the electrolytic cell provided that it contains electrolytes. However, it is preferable to add electrolytes such as a chloride for the purpose of successfully conducting the electrolysis. Sodium chloride (NaCl) or potassium chloride (KCl) may be used as the electrolytes.

For a better understanding of the invention, and to show how the same may be carried into effect, reference will now be made, by way of example only to the accompanying drawings, wherein:-

FIG. 1 is a cross-sectional view illustrating an example of an apparatus for use in the first process embodying the present invention described herein.

FIG. 2 is a cross-sectional view illustrating an example of the construction of an apparatus for use in the second process embodying the present invention described herein.

FIG. 3 is a cross-sectional view illustrating an example of the construction of an apparatus for use in the third process embodying the present invention described herein and:

FIG. 4 is a cross-sectional view illustrating another example of the construction of apparatus for use in the third process embodying the present invention described herein.

As illustrated in Fig. 1, an apparatus for use in one method embodying this invention includes a first electrolytic cell 1 and a second electrolytic cell 2. The first electrolytic cell 1 is so constructed that an anodic chamber 4 equipped with an anode 3 and a cathodic chamber 6 equipped with a cathode 5 are partitioned off by a cation-exchange membrane 7 (for example, Nefion 117, trade name, product of E.I. du Pont de Nemours & Co.). On the other hand, the second electrolytic cell 2 is so constructed that an anodic chamber 9 equipped with an anode 8 and a cathodic chamber 11 equipped with a cathode 10 are partitioned off by a like membrane 12 to the membrane 7.

To the top of the first electrolytic cell 1 is connected a raw water conduit 13 for feeding raw water containing a chloride such as sodium chloride or potassium chloride. The water conduit 13 branches in two, and the distal ends thereof are respective connections to the tops of the anodic chamber 4 and the cathodic chamber 6. The bottom of the anodic chamber 4 of the first electrolytic cell 1 is connected to the top of the cathodic chamber 11 of the second electrolytic cell 2 through a connecting pipe 14, while the bottom of the cathodic chamber 6 of the first electrolytic cell 1 is connected to the top of the anodic chamber 9 of the second electrolytic cell 2 through a connecting pipe 15. Take-off pipes 16 and 17 are connected to the bottoms of the anodic chamber 9 and cathodic chamber 11 of the second electrolytic cell 2, respectively.

The anode 3 and cathode 5 in the first electrolytic cell 1 and the anode 8 and cathode 10 in the second electrolytic cell 2 are separately connected to electric power sources (not illustrated) in such a manner that predetermined voltage can be applied between the anode 3 and the cathode 5 or between the anode 8 and the cathode 10. Further, additional devices (not illustrated) for adding an aqueous solution of a chloride may be provided on the water conduit 13, and the connecting pipes 14 and 15.

The ion-permeable membranes 7 and 12 may be in any form such as a woven fabric, nonwoven fabric or plastics film. Membranes having physical voids or pores or possessing a function that an electric charge can be transmitted and transferred like a solid electrolyte membrane can also be used. Examples of the membranes having physical voids or pores include microporous films of polymers such as polypropylene and polyethylene (for example, porous polyolefin film, "U-PORE", trade mark, product of UBE INDUSTRIES, LTD.), and nonwoven fabrics made of natural fibers or synthetic fibers. Typical examples of membranes having a function that an electric charge can be transmitted and transferred include ion-exchange membranes.

The membranes 7, 12 are preferably ion-exchange membranes having alkali resistance, such as membranes of fluororesins, because a hydroxide such as caustic soda (NaOH) or caustic potash (KOH) is formed from the chloride contained in the raw water, such as sodium chloride or potassium chloride, on the cathodic side in the first electrolysis step, so that the electrolysis solution becomes strongly alkaline. Examples of the fluororesins include perfluorosulfone resins.

In the apparatus illustrated in FIG. 1, the raw water containing the chloride is continuously fed to the anodic chamber 4 and cathodic chamber 6 of the first electrolytic cell 1 through the water conduit 13. The water fed to the cathodic chamber 6 is electrolyzed by voltage applied between the anode 3 and the cathode 5, while passing through the

cathodic chamber 6, thereby producing primary electrolyzed water on the cathodic side. The primary electrolyzed water on the cathodic side is then continuously withdrawn through the connecting pipe 15 and continuously fed to the anodic chamber 9 of the second electrolytic cell 2. The primary electrolyzed water obtained on the cathodic side is further electrolyzed by voltage applied between the anode 8 and the cathode 10 while passing through the anodic chamber 9, thereby preparing the electrolyzed functional water. The electrolyzed functional water is continuously withdrawn through the take-off pipe 16.

On the other hand, the raw water continuously fed to the anodic chamber 4 of the first electrolytic cell 1 is electrolyzed by the voltage applied between the anode 3 and the cathode 5 while passing through the anodic chamber 4, thereby producing primary electrolyzed water on the anodic side. The primary electrolyzed water on the anodic side is then continuously withdrawn through the connecting pipe 14 and continuously fed to the cathodic chamber 11 of the second electrolytic cell 2. The primary electrolyzed water obtained on the anodic side is further electrolyzed by the voltage applied between the anode 8 and the cathode 10 while passing through the cathodic chamber 11, thereby producing secondary electrolyzed water.

The secondary electrolyzed water contains chlorine and chlorine compounds such as hypochlorous acid produced by the first electrolysis, but its pH is changed to an alkaline pH by the second electrolysis in the cathodic chamber 11. Therefore, the chlorine compounds are stabilized to produce a bleaching and sterilizing solution, which is a by-product of the electrolyzed functional water. The bleaching and sterilizing solution is continuously withdrawn through the take-off pipe 17.

In the first electrolytic cell 1, the anodic chamber 4 and the cathodic chamber 6 are partitioned by the ion-permeable membrane 7, so that the primary electrolyzed water on the anodic side and the primary electrolyzed water on the cathodic side are not mixed with each other though electric charges are mutually transferred. In the second electrolytic cell 2, the anodic chamber 9 and the cathodic chamber 11 are also partitioned by the ion-permeable membrane 12, so that the electrolyzed functional water and the bleaching and sterilizing solution are not mixed with each other.

In the apparatus illustrated in FIG. 1, tap water containing added potassium chloride was continuously fed as the raw water through the raw water conduit 13 to undergo continuous electrolysis by applying voltage between the anode 3 and the cathode 5 in the first electrolytic cell 1 and between the anode 8 and the cathode 10 in the second electrolytic cell 2.

As a result, the electrolyzed functional water taken out through the take-out pipe 16 was found to contain hydrogen peroxide and have an oxidation-reduction potential of 600 to 1,100 mV, a pH of 6.4-9.6 and a concentration of residual chlorine of 5 to 12 ppm.

The electrolyzed functional water was added dropwise to a solution of potassium iodide (KI). As a result, the color of the solution turned brown, thereby confirming that iodine had been formed, and so the electrolyzed functional water has oxidizing ability. Besides, a solution of potassium permanganate ( $\text{KMnO}_4$ ) was added dropwise to the electrolyzed functional water. As a result, the solution turned transparent, thereby confirming that manganese ions ( $\text{Mn}^{2+}$ ) had formed from permanganate ions ( $\text{MnO}_4^-$ ), and so the electrolyzed functional water has reducing ability. As a result, it was strongly suggested that the electrolyzed functional water has oxidizing ability and reducing ability against strong oxidizing agents such as a permanganate ion, and hence contains hydrogen peroxide. From an electrochemical point of view, a peak considered to be attributable to hydrogen peroxide was observed by cyclic voltammetry. Accordingly, it may be considered that hydrogen peroxide had been formed.

In addition, the alkaline bleaching and sterilizing solution containing hypochlorous acid was withdrawn through the take-off pipe 17.

The electrolyzed functional water produced by the apparatus illustrated in FIG. 1 was then used to conduct a bactericidal test against *Fusarium. Oxysporum. f. sp cucumerinum* Owen. This test was conducted by preparing three suspensions containing *Fusarium. Oxysporum. f. sp cucumerinum* Owen at initial conidium densities of about  $1 \times 10^6$  spores/ml,  $1 \times 10^7$  spores/ml and  $1 \times 10^8$  spores/ml, respectively, diluting the suspensions to 1/10 separately with the electrolyzed functional water and sterile water, and spreading these diluted suspensions on respective media to culture them for predetermined numbers of days, thereby indicating whether *Fusarium. Oxysporum. f. sp cucumerinum* Owen grew or not. The results are shown in the following Table 1.

Table 1

	Initial conidium density (spores/ml)		
	$1 \times 10^6$	$1 \times 10^7$	$1 \times 10^8$
Electrolyzed functional water	++	+	±

+: Effective (slightly grew)

±: Effective though not marked (grew at a visually countable level)

Table 1 (continued)

	Initial conidium density (spores/ml)		
	1 x 10 <sup>6</sup>	1 x 10 <sup>7</sup>	1 x 10 <sup>8</sup>
Sterile water	-	-	-

- : Ineffective (grew in such a great amount as to be visually uncountable)

It is apparent from Table 1 that no bactericidal effect is observed with the sterile water, while the electrolyzed functional water has a clear effect on *Fusarium. Oxysporum. f. sp cucumerinum* Owen at an initial conidium density of 1 x 10<sup>7</sup> spores/ml or lower and a considerable effect at an initial conidium density of 1 x 10<sup>8</sup> spores/ml or lower.

Apparatus for use in a second method embodying the present invention will now be described, with reference to Fig. 2. The illustrated apparatus includes an electrolytic cell 24 having two chambers 22 and 23 partitioned by a membrane 21 made of a cation-exchange membrane (for example, Nafion 117, trade name, product of E. I. du Pont de Nemours & Co.). Electrodes 25 and 26 obtained by supporting platinum on a titanium mesh base are provided in the chambers 22 and 23, respectively, and are connected to an electric power source 28 through an external circuit 27. The electrodes 25, 26 are so constructed that their polarities can be changed over by switches 29 and 30 provided in the external circuit 27.

In the apparatus illustrated in FIG. 2, the electrodes 25, 26 were first connected to the electric power source 28 through the switches 29, 30 so as to use the electrodes 25 and 26 as an anode and a cathode, respectively, and raw water (tap water) W containing sodium chloride as an electrolyte was fed to the chambers 22, 23. Voltage of 5 V was then applied between the electrodes 25 and 26 to conduct a first electrolysis according to a predetermined quantity of electric charge.

A second electrolysis was then conducted under the same conditions as in the first electrolysis except that the switches 29, 30 were changed over, thereby reversing the polarities of electric currents applied to the electrodes 25, 26 so as to use the electrodes 25 and 26 as a cathode and an anode, respectively. As a result, electrolyzed functional water containing hydrogen peroxide was obtained from the anodic side (the side of the chamber 23 and electrode 26) in the second electrolysis.

The physical properties of the electrolyzed water obtained from the anodic and cathodic sides in the above first and second electrolyses are shown in the following Table 2.

Table 2

		Anodic side	Cathodic side
First electrolysis	Oxidation-reduction potential (mV)	1185	-855
	pH	2.53	11.73
	Concentration of residual chlorine (ppm)	40	0.3
Second electrolysis	Oxidation-reduction potential (mV)	1106	52
	pH	9.85	9.60
	Concentration of residual chlorine (ppm)	1.5	30

It is apparent from Table 2 that the electrolyzed functional water having high oxidation-reduction potential and low concentration of residual chlorine is obtained from the anodic side (the side of the chamber 23 at which electrode 26 is located in the second electrolysis).

It was confirmed by the coloring of a potassium iodide solution and the decolorising of a potassium permanganate solution that the electrolyzed functional water obtained from the anodic side in the second electrolysis contains hydrogen peroxide.

After first electrolysis was then conducted under the same conditions as described above by means of the apparatus illustrated. In FIG. 2, second electrolysis was performed by changing over the switches 29, 30 to reverse the polarities of electric currents applied to the electrodes 25, 26 so as to use the electrodes 25 and 26 as a cathode and an anode, respectively, and moreover changing the quantity of electric charge to 1.2 times, 1.5 times or 2.0 times as much as the quantity of electric charge used in the earlier procedure.

Physical properties of the electrolyzed functional water obtained from the anodic side (the side of the chamber 23 and electrode 26) in the second electrolysis are shown in the following Table 3.

Table 3

Quantity of electric charge (times)	Oxidation-reduction potential (mV)	pH	Concentration of residual chlorine (ppm)
1.0 (second embodiment)	1106	9.85	1.5
1.2	1030	5.73	2.0
1.5	1018	3.54	2.0
2.0	1092	2.78	2.5

It is apparent from Table 3 that various kinds of electrolyzed functional water having different physical properties can be obtained by changing electrolytic conditions (such as quantity of electric charge) in the second electrolysis. In particular, it is apparent that the pH of the electrolyzed functional water can be controlled over a wide range from an acidic pH to a weakly alkaline pH by controlling the quantity of electric charge as described above.

An electrolyzed functional water was then produced by using an apparatus in which the volume of each of the chambers 22, 23 in the electrolytic cell 24 illustrated in FIG. 2 was 2 liters, feeding tap water containing 0.8 g/liter (corresponding to 0.013 mol calculated as NaCl) of common salt as raw water, and applying 0.8 A of an electric current between the electrodes 25 and 26 at 27.2°C, thereby conducting first electrolysis and second electrolysis each for 25 minutes by constant-current electrolysis. Physical properties of the electrolyzed water obtained from the anodic and cathodic sides in the above first and second electrolysis are shown in the following Table 4.

Table 4

		Anodic side	Cathodic side
First electrolysis	Oxidation-reduction potential (mV)	1066	-865
	pH	2.65	11.34
	Concentration of residual chlorine (ppm)	7	-
Second electrolysis	oxidation-reduction potential (mV)	252	-65
	pH	5.26	10.28
	Concentration of residual chlorine (ppm)	5	6

Using the apparatus illustrated in FIG. 2, electrolyzed functional water was then produced under the same conditions as in the case of Table 4. As a result, electrolyzed functional water having an oxidation-reduction potential of 160 mV, a pH of 6.01 and a concentration of residual chlorine of 6 ppm was obtained.

The electrolyzed functional water thus obtained was used to conduct a bactericidal test against various kinds of bacteria. In this bactericidal test, suspensions of a gram-positive bacterium (*Staphylococcus aureus* IFO 13276), a gram-negative bacterium (*Escherichia coli* ATCC 14621) and a spore bearing bacterium (*Bacillus subtilis* ATCC 6633, only spore) were separately inoculated into portions of the electrolyzed functional water obtained from the anodic side (the side of the chamber 23 with electrode 26) in the above second electrolysis so as to give cell counts of about  $1 \times 10^3$  cells/ml,  $1 \times 10^5$  cells/ml and  $1 \times 10^7$  cells/ml. samples being prepared for every bacterium. Each of the samples was cultured at room temperature ( $25 \pm 2^\circ\text{C}$ ). After 30 seconds, 1 minute and 10 minutes from the inoculation, 1 ml of each sample was taken out to count the number of viable cells (the number of colonies) by an agar plate dilution method (culture for 48 hours at  $37^\circ\text{C}$  on a nutrient agar medium). The viable cell counts were determined by a conventional counting method either visually or through a microscope (magnifier).

The results of the determination of viable cell counts are shown in Table 5. The numerical values shown in Table 5 are average values of 3 agar plates.

Table 5

	Quantity inoculated (cells/ml)	Elapsed time after inoculation		
		30 sec.	1 min.	10 min.
<i>Staphylo- coccus aureus</i>	$4.2 \times 10^3$	0	0	0
	$4.2 \times 10^5$	0	0	0
	$4.2 \times 10^7$	4	2	1
<i>Escherichia coli</i>	$9.4 \times 10^3$	0	0	0
	$9.4 \times 10^5$	0	0	0
	$9.4 \times 10^7$	$8.6 \times 10^2$	$1.6 \times 10$	1
<i>Bacillus subtilis</i>	$1.6 \times 10^3$	$3.7 \times 10$	$2.3 \times 10$	6
	$1.6 \times 10^5$	$2.2 \times 10^4$	$3.7 \times 10^3$	0
	$1.6 \times 10^7$	$2.1 \times 10^6$	$4.5 \times 10^5$	$5.6 \times 10^4$

It is apparent from Table 5 that the electrolyzed functional water has sufficient bactericidal effects even after 30 seconds from the inoculation and hence has an immediate effect on the bacteria.

Apparatus for use in a third method embodying the present invention will now be described with reference to Fig. 3. Here, the production apparatus includes an electrolytic cell 34 equipped with an anode 32, a cathode 33 and an ion-permeable membrane 31 between them. The anode 32 and the cathode 33 are connected to a power source (not illustrated). The electrolytic cell 34 is provided with a raw water feeding conduit 35 for continuously feeding raw water containing a chloride such as sodium chloride or potassium chloride as electrolytes to the top of a cathodic chamber 33a, in which the cathode 33 is provided, and includes an electrolyzed water feeding conduit 36, which connects the bottom of the cathodic chamber 33a to the top of an anodic chamber 32a, in which the anode 32 is provided, and continuously feeds the electrolyzed water taken out from the cathodic chamber 33a to the anodic chamber 32a. The cell also includes an electrolyzed functional water take-off conduit 37 for continuously withdrawing electrolyzed functional water containing hydrogen peroxide from the bottom of the anodic chamber 32a.

The ion-permeable membrane 31 may be in any form such as a woven fabric, nonwoven fabric or plastics film (polymer film) as described above, and a fabric having physical voids or pores or possessing the property of enabling an electric charge can be transmitted and transferred therethrough like a solid electrolyte membrane is preferably used. Examples of such membranes include ion-exchange membranes. The membrane is preferably an ion-exchange membrane having alkali resistance such as a membrane of a fluororesin for the above-described reason.

Used as the anode 32 and the cathode 33 are electrodes made of a titanium base coated with platinum oxide or indium oxide. An electric current is applied to the anode 32 and the cathode 33 from a power source to electrolyze the water within the electrolytic cell 34.

In this embodiment, raw water containing chloride such as sodium chloride or potassium chloride is first fed to the cathodic chamber 33a through the raw water feeding conduit 35. When the raw water has filled the cathodic chamber 33a, it is then fed to the anodic chamber 32a through the electrolyzed water feeding conduit 36. When both electrolytic chambers 32a, 33a are filled with the raw water, an electric current is applied to the anode 32 and the cathode 33 from a power source to initiate electrolysis.

By this electrolysis, hydrogen is generated and hydroxide ions ( $\text{OH}^-$ ) are generated by electrolysis mainly of the water in the cathodic chamber 33a, thereby obtaining alkaline electrolyzed water. In the anodic chamber 32a on the other hand, oxygen ( $\text{O}_2$ ) and hydrogen ions are generated by electrolysis mainly of the water at the initial stage of the electrolysis, as with electrolysis of water generally. However, at the same time, chloride ion ( $\text{Cl}^-$ ) derived from the electrolyte is oxidized into chlorine ( $\text{Cl}_2$ ). As a result, acidic electrolyzed water containing chlorine is obtained in the anodic chamber 32a at the initial stage of the electrolysis and is withdrawn through the electrolyzed functional water taking-out conduit 37.

In this embodiment, the raw water is continuously fed to the cathodic chamber 33a through the raw water feeding conduit 35. When the electrolysis is continuously conducted, therefore, the alkaline electrolyzed water generated in the cathodic chamber 33a is fed to the electrolytic chamber 32a on the anodic side through the electrolyzed water feeding conduit 36, and the acidic electrolyzed water produced at the initial stage of the electrolysis in the anodic chamber 32a is replaced by the alkaline electrolyzed water produced in the cathodic chamber 33a.

As the electrolysis is further continued, the acidic electrolyzed water in the anodic chamber 32a is completely replaced by the alkaline electrolyzed water, and the alkaline electrolyzed water taken out of the cathodic chamber 33a

is continuously fed to the anodic electrolytic chamber 32a after this, whereby the electrolyzed water is electrolyzed together with new raw water fed to the cathodic chamber 33a. At this stage, the same reaction as described above takes place in the cathodic chamber 33a, and so hydrogen and a hydroxide ion ( $\text{OH}^-$ ) are generated, thereby yielding alkaline electrolyzed water. In the anodic chamber 32a, however, the alkaline electrolyzed water is electrolyzed, whereby hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and oxygen are generated from the hydroxide ions contained in the electrolyzed water. At this time,  $\text{Cl}^-$  (chloride ion) contained in the alkaline electrolyzed water is simultaneously oxidized, whereby hypochlorous acid is generated as a chlorine component.

As a result, after the acidic electrolyzed water in the anodic electrolytic chamber 32a is completely replaced by the alkaline electrolyzed water, electrolyzed functional water containing hydrogen peroxide can be continuously withdrawn from the anodic chamber 32a through the electrolyzed functional water take-off conduit 37.

Electrolysis was performed by using an apparatus having the same construction as that illustrated in FIG. 3, in which the volume of each of the electrolytic chambers 32a and 33a was 20 liters, continuously feeding raw water containing 0.8 g/liter (corresponding to 0.013 mol calculated as NaCl) of common salt at a flow rate of 0.5 liter/min through the raw water feeding conduit 35, and applying 2.5 A of an electric current between the anode 32 and the cathode 33. As a result, acidic electrolyzed water formed in the anodic chamber 32a at the initial stage of the electrolysis was almost completely replaced by alkaline electrolyzed water formed in the cathodic chamber 33a in about 10 seconds after the initiation of the electrolysis. stable electrolyzed functional water was obtained after about 30 seconds in view of the volume of the pipe arrangement. At this stage and later, the whole amount of the raw water fed through the raw water feeding conduit 35 could be withdrawn as the electrolyzed functional water containing hydrogen peroxide through the electrolyzed function water take-off conduit 37. No chlorine gas was detected during this electrolysis.

The values of pH just after the electrolysis, oxidation-reduction potential (ORP) against a silver-silver chloride standard electrode, and available residual chlorine concentrations of the electrolyzed functional water produced under the electric current of 2.5 A are shown in Table 6.

Another electrolysis was then performed in the same manner as described above except that 20.0 A of an electric current were applied between the anode 32 and the cathode 33. The pH just after the electrolysis, oxidation-reduction potential against a silver-silver chloride standard electrode, and available residual chlorine concentration of the electrolyzed functional water produced under the electric current of 20.0 A are shown in Table 6.

Table 6

	Current upon electrolysis (A)	
	2.5	20.0
pH	7.68	7.54
oxidation-reduction potential (mV)	415	709
concentration of available residual chlorine (ppm)	15	70

As is apparent from Table 6, the production process of this embodiment can provide electrolyzed functional water containing hydrogen peroxide. When the electric current was 2.5 A as compared with when the electric current was 20.0 A, it is understood that the concentration of the available residual chlorine increases as the electric current increases, and the concentration of the available residual chlorine can be controlled by the electric current. The reason for this is that the oxidation reaction of water and the oxidation reaction of the chloride ions ( $\text{Cl}^-$ ) take place at the same time, and so the concentration of the available residual chlorine can be increased by increasing the intensity of the electric current.

Finally another form of apparatus for use in the third method embodying the present invention will be described with reference to Fig. 4. Here, the production apparatus includes an electrolytic cell 44 equipped with a first electrode 42, a second electrode 43 and an ion-permeable membrane 41 between them. The electrolytic cell 44 includes a first electrolytic chamber 42a, in which the first electrode 42 is provided, and a second electrolytic chamber 43a, in which the second electrode 43 is provided. Both said electrodes 42, 43 are connected to an external DC power source 46 through a circuit 45, and are so set up that their polarities can be changed over by switches 47 and 48.

The electrolytic cell 44 is so constructed that a flow path for a raw water or electrolyzed water fed to the electrolytic chamber 42a or 43a can be changed over according to the polarities of the electrodes 42, 43, which are changed over by the switches 47, 48. A first flow path is adapted to the case where the first electrode 42 is a cathode, and comprises a first raw water feeding conduit 51 for continuously feeding raw water containing chloride such as sodium chloride or potassium chloride as an electrolyte to the top of the first electrolytic chamber 42a through a change-over valve 49 and a connecting pipe 50; a first electrolyzed water feeding conduit 54 for continuously feeding the electrolyzed water withdrawn from the bottom of the first electrolytic chamber 42a to the top of the second electrolytic chamber 43a through

a change-over valve 52 and a connecting pipe 53, and a first electrolyzed functional water take-off conduit 55 for continuously withdrawing electrolyzed functional water containing hydrogen peroxide from the bottom of the second electrolytic chamber 43a. On the other hand, a second flow path is available for the case where the second electrode 43 is a cathode, and comprises a second raw water feeding conduit 56 for continuously feeding the raw water to the top of the second electrolytic chamber 43a through the change-over valve 52 and the connecting pipe 53, a second electrolyzed water feeding conduit 57 for continuously feeding the electrolyzed water withdrawn from the bottom of the second electrolytic chamber 43a to the top of the first electrolytic chamber 42a through the change-over valve 49 and the connecting pipe 50, and a second electrolyzed functional water take-off conduit 58 for continuously withdrawing electrolyzed functional water containing hydrogen peroxide from the bottom of the first electrolytic chamber 42a.

In FIG. 4, the first flow path is illustrated by solid-line arrows, and the second flow path is illustrated by broken-line arrows. The common flow paths for the raw water and drain are associated with double-line arrows.

The first raw water feeding conduit 51 and the second raw water feeding conduit 56 branch off from a main raw water feeding conduit 59 on their upstream side. The first electrolyzed functional water take-off conduit 55 and the second electrolyzed functional water take-off conduit 58 are so constructed that they can be connected to a drain conduit 62 by changing over change-over valves 60 and 61.

In the apparatus illustrated in FIG. 4, in the case where the first electrode 42 is used as a cathode by appropriately setting the switches 47, 48, the flow path can be changed over to the first flow path (illustrated by the solid-line arrows in FIG. 4) by turning the change-over valve 49 so as to connect the first raw water feeding conduit 54 to the connecting pipe 50, turning the change-over valve 52 so as to connect the first electrolyzed water feeding conduit 54 to the connecting pipe 53, turning the change-over valve 60 so as to be able to withdraw the electrolyzed functional water through the first electrolyzed functional water taking-out conduit 55, and closing the change-over valve 61. Then, the raw water is continuously fed through the first raw water feeding conduit 51 to conduct electrolysis, whereby hydrogen and a hydroxide ion ( $\text{OH}^-$ ) are generated by electrolysis mainly of the water in the first electrolytic chamber 42a to obtain alkaline electrolyzed water. In the second electrolytic chamber 43a on the other hand, oxygen ( $\text{O}_2$ ) is generated and hydrogen ions are formed by electrolysis mainly of the water at the initial stage of the electrolysis, and at the same time, chloride ions ( $\text{Cl}^-$ ) derived from the electrolyte are oxidized into chlorine ( $\text{Cl}_2$ ), with acidic electrolyzed water containing chlorine being obtained. When the electrolysis is continuously conducted to replace the acidic electrolyzed water formed at the initial stage of the electrolysis by the alkaline electrolyzed water formed in the first electrolytic chamber 42a, however, the alkaline electrolyzed water is electrolyzed in the second electrolytic chamber 43a, with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and oxygen being formed from the hydroxide ions contained in the electrolyzed water. At this time,  $\text{Cl}^-$  (chlorine ions) contained in the alkaline electrolyzed water is simultaneously oxidized, whereby hypochlorous acid is formed as a chlorine component. As a result, after the acidic electrolyzed water in the second electrolytic chamber 43a is completely replaced by the alkaline electrolyzed water, electrolyzed functional water containing hydrogen peroxide can be continuously withdrawn from the second electrolytic chamber 43a through the first electrolyzed functional water take-off conduit 55.

In the apparatus illustrated in FIG. 4, the polarities of both said electrodes 42, 43 are reversed to remove scale adhered to the electrodes 42, 43 after electrolysis has been continuously conducted for a predetermined period of time. In the case where the polarities are reversed by changing over the switches 47, 48 to use the second electrode 43 as a cathode, the flow path is changed over to the second flow path (illustrated by the broken-line arrows in FIG. 4) by turning the change-over valve 52 so as to connect the second raw water feeding conduit 56 to the connecting pipe 53, turning the change-over valve 49 so as to connect the second electrolyzed water feeding conduit 57 to the connecting pipe 50, turning the change-over valve 61 so as to withdraw the electrolyzed functional water through the second electrolyzed functional water take-off conduit 58, and closing the change-over valve 60. Then, the raw water is continuously fed through the second raw water feeding conduit 56 to conduct electrolysis, with alkaline electrolyzed water being obtained in the second electrolytic chamber 43a in contrast with the case of the first flow path. In the first electrolytic chamber 42a, the acidic electrolyzed water containing chlorine is obtained at the initial stage of the electrolysis. After the acidic electrolyzed water is completely replaced by the alkaline electrolyzed water formed in the second electrolytic chamber 43a by continuing the electrolysis, electrolyzed functional water containing hydrogen peroxide can be continuously withdrawn from the first electrolytic chamber 42a through the second electrolyzed functional water take-off conduit 58.

By using the apparatus illustrated in Fig. 4, therefore, the scale deposited on the electrodes 42, 43 can be removed by periodically reversing the polarities of the electrodes 42, 43 to prevent the gradual decrease of electrolysis efficiency, and moreover electrolyzed functional water containing hydrogen peroxide can be continuously withdrawn except at the initial stage of the electrolysis and just after the reversing of polarities.

In the apparatus illustrated in FIG. 4, after completion of the production of a predetermined amount of the electrolyzed functional water, the change-over valves 60, 61 are turned to connect the electrolyzed functional water take-off conduits 55, 58 to the drain conduit 62, whereby the raw water or the electrolyzed water remaining in the electrolytic chamber 42a or 43a can be discharged through the drain conduit 62.

In the respective embodiments described above, the oxidation-reduction potential of the electrolyzed water formed considerably varies from one embodiment to another. However, the oxidation-reduction potential itself is not always directly to be taken as a pointer to the bactericidal effect because even if chemical species rich in oxidizing ability are present in plenty in a certain solution, the total oxidation-reduction potential appears low when a considerable number of chemical species low in oxidation-reduction potential is present in the solution.

In each of the above-described embodiments, the chloride is added as an electrolyte to the raw water fed to the electrolytic cell. However, the electrolyte is not limited to chloride, and  $\text{Na}_2\text{SO}_4$  and/or other electrolytes may be added to obtain electrolyzed water containing hydrogen peroxide from the anodic side in the second electrolyzing step like the case of the chloride. In this case, neither chlorine nor hypochlorous acid is present in the resultant electrolyzed water.

## Claims

1. A process for producing electrolyzed functional water which comprises:-

a first electrolyzing step of continuously feeding water containing electrolyte to an electrolytic cell equipped with an anode, a cathode and an ion permeable membrane therebetween to electrolyse it,  
a second electrolyzing step of subjecting to electrolysis, in the anodic side of an electrolytic cell equipped with an anode, a cathode and an ion permeable membrane therebetween, an electrolyte which is electrolyte to be found in the cathodic side of the electrolytic cell of the first electrolyzing step after water fed to said cell has been electrolysed,  
and withdrawing electrolyzed functional water from the anodic side used in the second electrolyzing step after water in said side has taken part in electrolysis in said second electrolyzing step.

2. A process according to claim 1 wherein the second electrolyzing step is carried out on the electrolyzed water obtained on the cathodic side of the electrolytic cell used in the first electrolyzing step, which electrolyzed water is continuously withdrawn from the cathodic side of said electrolytic cell and continuously fed to the anodic side of a second electrolytic cell in which it is subjected to the second electrolyzing step,

and wherein the electrolyzed functional water is continuously withdrawn from the anodic side of the second electrolytic cell.

3. The process according to claim 2, wherein electrolyzed water obtained in the anodic side of the electrolytic cell used in the first electrolyzing step is continuously withdrawn and fed to the cathodic side of the second electrolytic cell, and is electrolyzed there in the second electrolyzing step.

4. The process according to claim 1 wherein, after carrying out of the first electrolyzing step on water fed to the electrolytic cell, the polarities of the cell are reversed and the second electrolyzing step then comprises conducting electrolysis of the then existing contents of the electrolytic cell and is followed by the withdrawal of electrolyzed functional water from the side of the cell which is the anodic side in the second electrolyzing step.

5. The process according to any preceding claim, which includes a step of controlling current density of electrolysis to adjust pH of electrolyzed functional water obtained to be between 3.5 and 10.5.

6. The process according to claim 1 wherein the water containing electrolyte is fed continuously to the cathodic side of a said electrolytic cell containing electrolyte at the anodic side thereof and undergoes electrolysis, and wherein electrolyzed water is continuously withdrawn from the cathodic side of the electrolytic cell and fed to the anodic side of the electrolytic cell to be electrolyzed further as new water containing electrolyte is fed to the cathodic side and electrolyzed there, whereby said first and second electrolyzing steps take place simultaneously in the electrolytic cell, with electrolyzed functional water being withdrawn continuously from the anodic side of the electrolytic cell.

7. The process according to any preceding claim wherein the electrolyte contained in the water is chloride.

8. The process according to claim 7, wherein the electrolyte contained in the water is sodium chloride and/or potassium chloride.

9. The process according to any preceding claim wherein the concentration of the electrolyte contained in the water is in a range from 0.001 to 1 mol/liter.

10. An apparatus for producing electrolyzed functional water, which comprises an electrolytic cell (34) equipped with two electrodes (32,33) separated by an ion-permeable membrane (31), a water feeding means (35) for continuously feeding water containing electrolyte to one side (33a) of the electrolytic cell containing one said electrode (33), an electrolyzed water feeding means (36) for continuously feeding water electrolyzed at the electrode (33) at said one side (33a) of the electrolytic cell (34) to the other side (32a) of the electrolytic cell (34) to undergo further electrolysis at the other said electrode (32) and a take-off means (37) for continuously withdrawing electrolyzed functional water from the side (32a) of the electrolytic cell (34) at which the further electrolysis has occurred, in which apparatus said one electrode (33) and the other said electrode (32) are electrically connected to act as a cathode and an anode respectively.

11. An apparatus according to claim 10, which has the polarities of said electrodes reversible:

and which comprises a first flow path comprising a first water feeding means (51) for continuously feeding water containing electrolyte to a side (42a) of an electrolytic cell (44) containing one said electrode (42) when said one electrode is used as a cathode, a first electrolyzed water feeding means (54) for continuously feeding the electrolyzed water from the side (42a) containing the first electrode (42) to the side (43a) containing the other electrode (43), and a first electrolyzed functional water take-out means (55) for continuously withdrawing electrolyzed functional water from the other side (43a) of the electrolytic cell:

a second flow path comprising a second water feeding means (56) for continuously feeding water containing electrolyte to the side (43a) of said electrolytic cell (44) containing the other electrode (43) when the other electrode is used as a cathode, a second electrolyzed water feeding means (57) for continuously feeding the electrolyzed water from the side (43a) containing the other electrode (43) to the side containing said one electrode (42), and a second electrolyzed functional water take-out means (58) for continuously withdrawing electrolyzed functional water from the side (42a) containing said one electrode (42); and

a change-over means (49,52,60,61) for changing a flow path over to the first flow path when the said one electrode (42) is used as a cathode or over to the second flow path when the other electrode (43) is used as a cathode.

FIG. 1

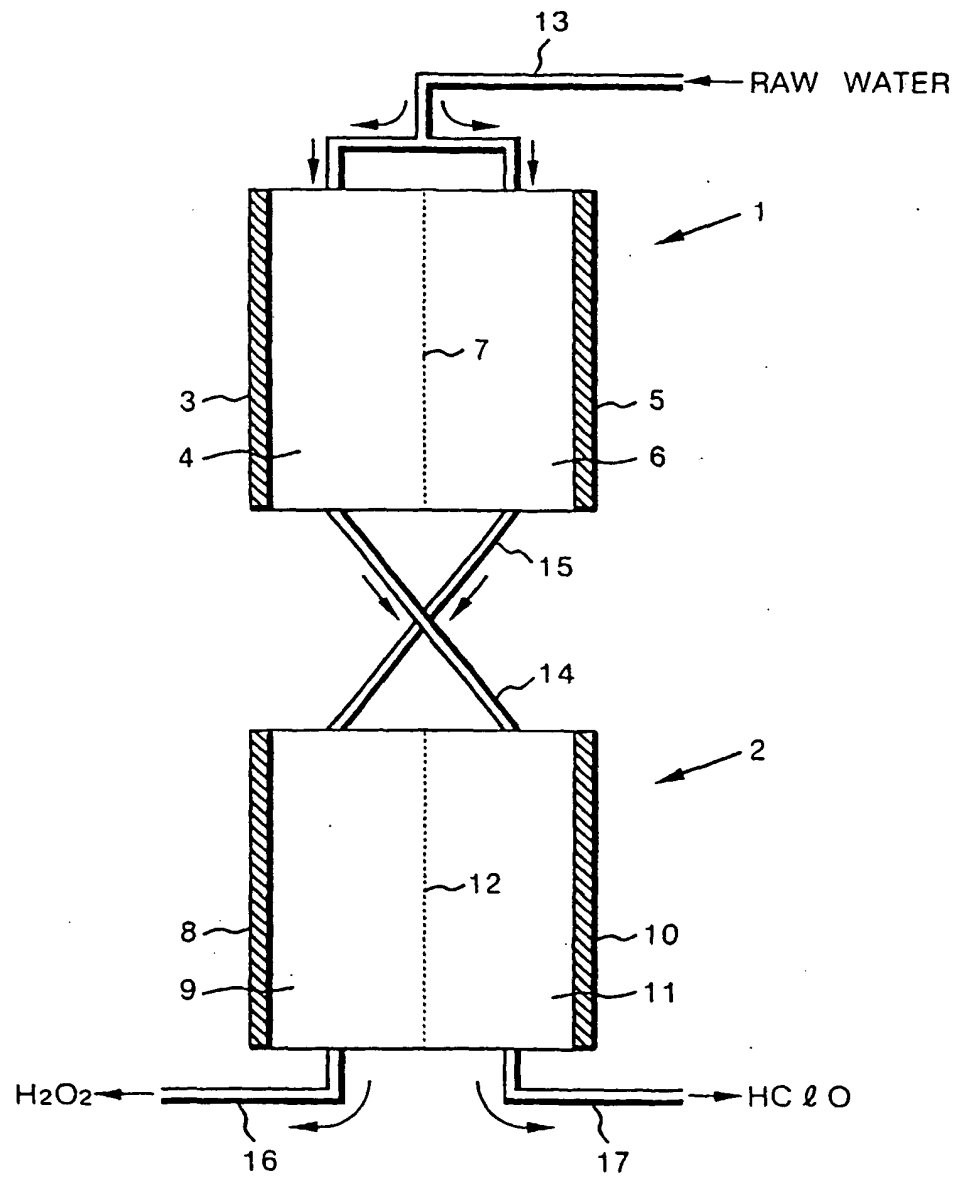


FIG. 2

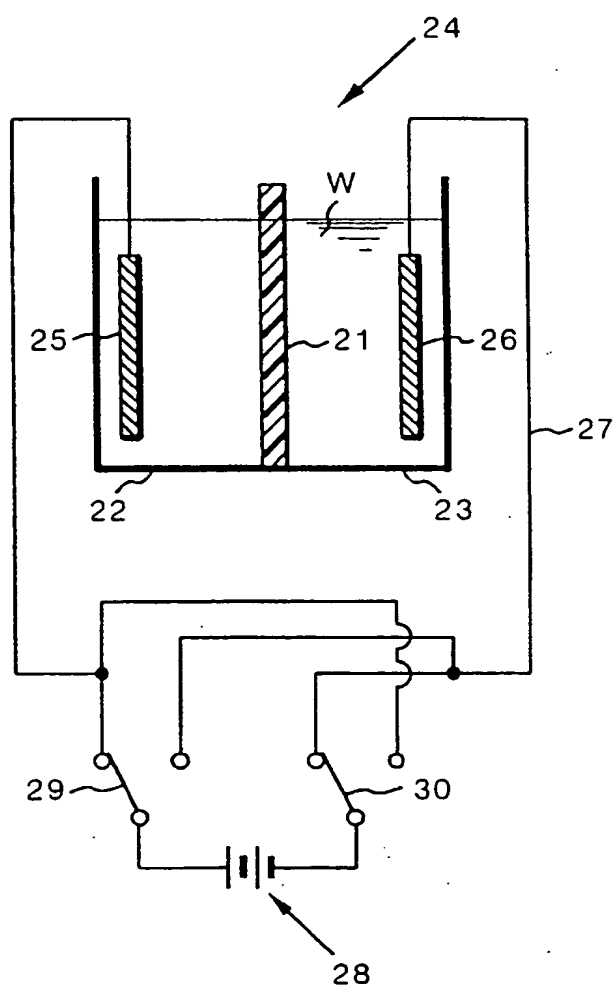


FIG. 3

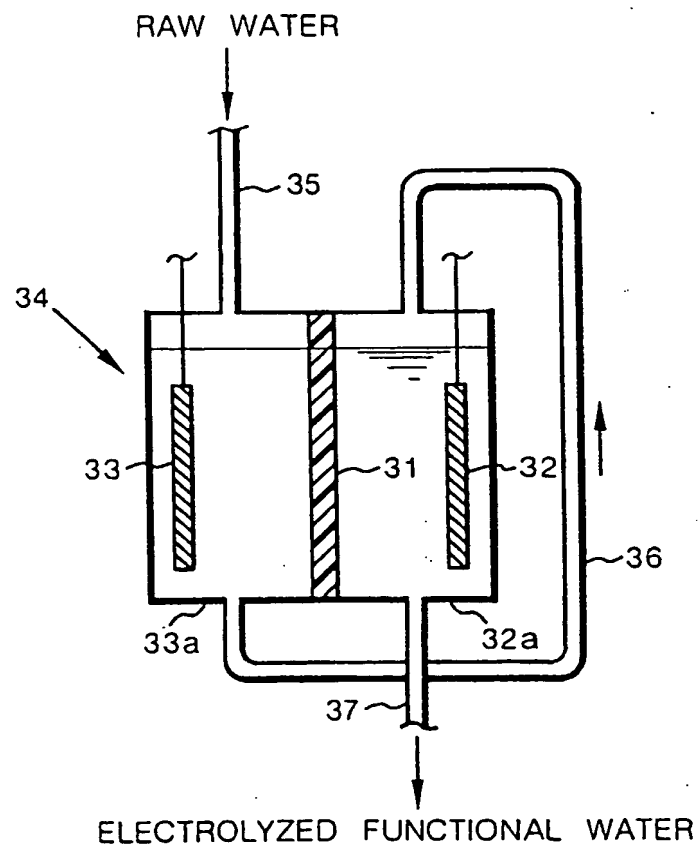
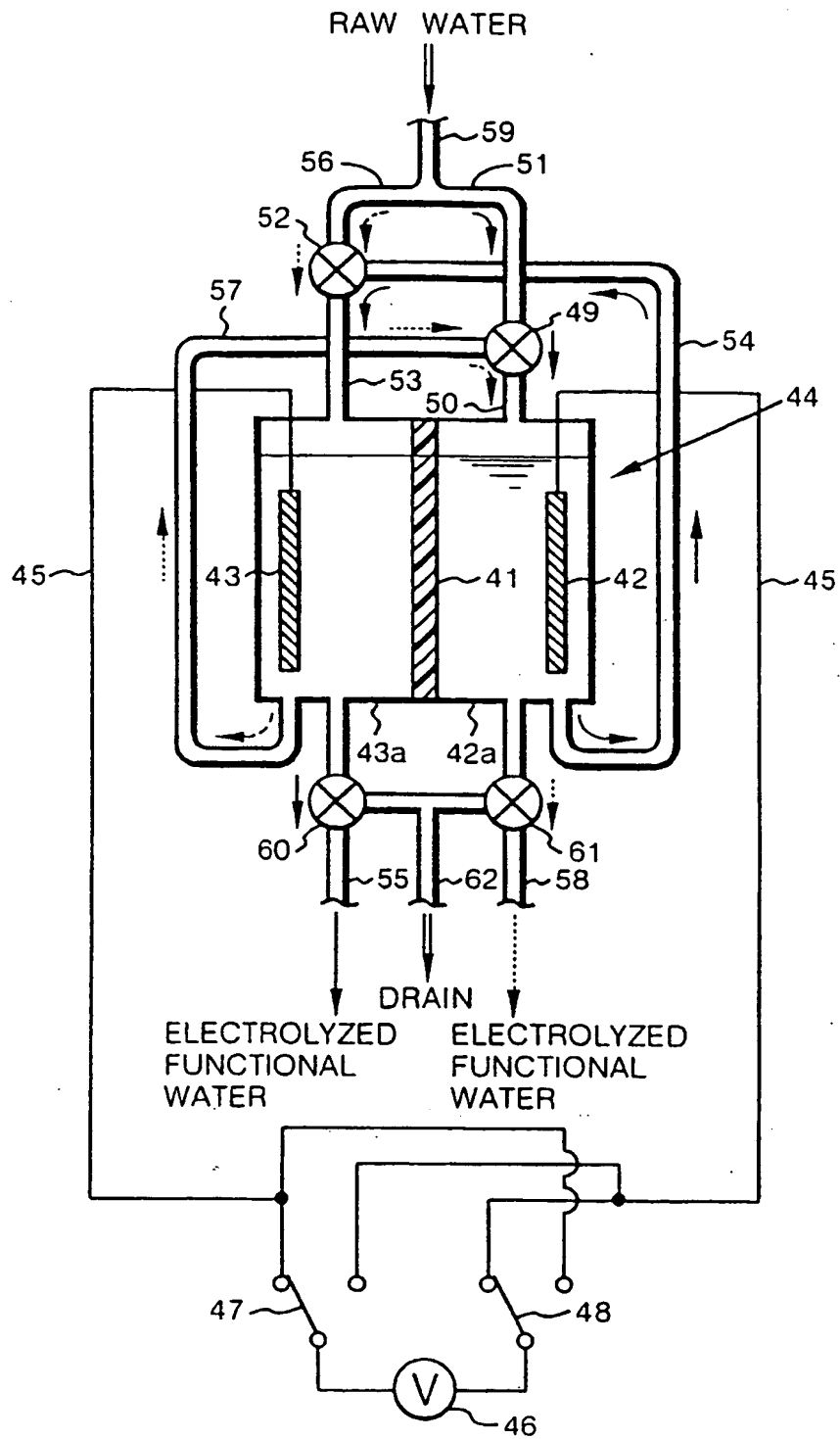
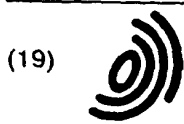


FIG. 4





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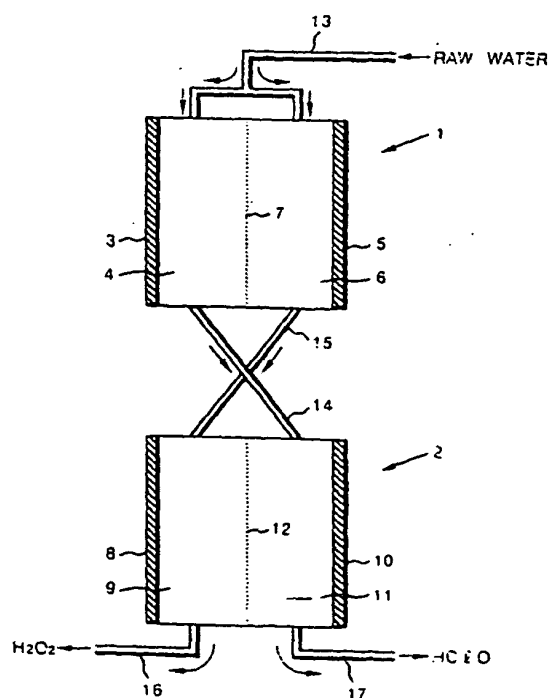
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(54) Process and apparatus for the production of electrolyzed water

(57) Electrolyzed functional water is produced by a two stage electrolysis. There is a first electrolyzing step of continuously feeding water containing electrolyte to an electrolytic cell (1) equipped with an anode (3), a cathode (5) and an ion permeable membrane (7) therebetween to electrolyze it and a second electrolyzing step of subjecting to electrolysis, in the anodic side (9) of an electrolytic cell (2) equipped with an anode (8), a cathode (10) and an ion permeable membrane (12) therebetween, an electrolyte which is electrolyte to be found in the cathodic side (6) of the electrolytic cell (1) of the first electrolyzing step after water fed to said cell has been electrolyzed. Electrolyzed functional water is withdrawn from the anodic side (9) used in the second electrolyzing step after water in this side has taken part in electrolysis in the second electrolyzing step.

FIG. 1





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# EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
E	WO 98 13304 A (BORWICK ROBERT NORMAN ; STOLLARD ROSALYN JEAN (GB); ENIGMA UK LTD) 2 April 1998 * claims 1,7 * * page 3, line 20 - line 21 *	1,6-8,10	C02F1/461
P,X	US 5 628 888 A (BAKHIR ET AL) 13 May 1997 * figures 2,4 * * column 4, line 54 - line 55 *	1,6-10	
X	PATENT ABSTRACTS OF JAPAN vol. 095, no. 002, 31 March 1995 -& JP 06 312183 A (SHINKO PANTEC CO LTD). 8 November 1994 * abstract; figures 1,3,7A,7B *	1-4	
X	DE 43 30 518 A (BLASCHKE MANFRED DR RER NAT ; JANIETZ PETER JOHANNES DR SC N (DE);) 9 March 1995 * page 3, line 25 - line 28 * * page 3, line 55 - page 4, line 49 * * figure 1 *	1-3	
X	PATENT ABSTRACTS OF JAPAN vol. 096, no. 011, 29 November 1996 & JP 08 192158 A (MATSUSHITA ELECTRIC IND CO LTD). 30 July 1996 * abstract: figure *	1,2	
X	PATENT ABSTRACTS OF JAPAN vol. 095, no. 007, 31 August 1995 & JP 07 100463 A (TATSUO OKAZAKI). 18 April 1995 * abstract: figure *	1,4	
X	EP 0 474 936 A (ISRAEL ATOMIC ENERGY COMM) 18 March 1992 * claims; figure 3A *	10 1,6	
A			
		-/--	
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>28 August 1998</b>	Examiner <b>Ruppert, G</b>
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document		T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons S: member of the same patent family, corresponding document	

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US 5 057 198 A (BOCHKAREV ET AL) 15 October 1991	10	
A	* column 4, line 62 - column 5, line 26; figure 4 *	1.6	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>28 August 1998</b>	Examiner <b>Ruppert, G</b>
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date O : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
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